Thermodynamics of Wax Precipitation in Petroleum Mixtures

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A thermodynamic framework is developed for calculating wax precipitation in petroleum mixtures over a wide temperature range. The framework uses the experimentally supported assumption that precipitated wax consists of several solid phases; each solid phase is described as a pure component or pseudocomponent that does not mix with other solid phases. Liquid-phase properties are obtained from an equation of state. Calculated wax-precipitation data are in excellent agreement with experimental results for binary and multicomponent hydrocarbon mixtures, including petroleum.

Introduction

The broad volatility and melting-point range of hydrocarbon components found in petroleum causes formation of vapor, liquid, and solid phases in response to changes in pressure, temperature, or composition. When the temperature falls, heavy hydrocarbon components in the liquid and vapor may precipitate as wax crystals. In the petroleum industry, wax precipitation is undesirable because it may cause plugging of pipelines and process equipment. Wax precipitation is an old problem (Fagin, 1945; Goldman and Nathan, 1957; Ford et al., 1965) but only recently have attempts been made to develop a thermodynamic description.

Published methods for describing wax precipitation are often in poor agreement with experimental data; they tend to overestimate the amount of wax at temperatures below the cloud-point temperature, which is the temperature where wax first begins to precipitate. Computational tools based on regular-solution theory of mixtures as well as on equations of state (EOS) have been proposed to model wax precipitation (cf. Won, 1986, 1989; Hansen et al., 1988; K. S. Pedersen et al., 1991; Pedersen, 1993; Erickson et al., 1993). All of these methods assume that all the compounds that precipitate from the liquid or vapor form a solid solution. However, spectroscopic and calorimetric studies reported in the last few years by Snyder et al. (1992, 1993, 1994) and W. B. Pedersen et al. (1991) suggest that large hydrocarbons are mutually insoluble in the solid state.

To illustrate previous work, Figure 1 shows the essential thermodynamic equations for a three-phase flash calculation for a waxy crude oil mixture, assuming that only one solid phase is present; that phase is assumed to be a solid solution. At fixed temperature and pressure, a liquid phase \( l \) may coexist in equilibrium with a vapor phase \( v \) and a solid phase \( s \).

\[
\begin{align*}
 f_i^v &= \varphi_i^v y_i \mu_i P \\
 f_i^l &= \gamma_i^l x_i f_i^\text{pure} \\
 f_i^s &= \varphi_i^s x_i f_i^\text{pure} \\
 \text{or} \\
 f_i^v &= \gamma_i^l x_i f_i^\text{pure} \\
 f_i^l &= \varphi_i^s x_i f_i^\text{pure}
\end{align*}
\]

Figure 1. Typical vapor–liquid–solid-solution model for wax precipitation used by previous authors.
where \( f \) is the fugacity and \( N \) is the number of components. An EOS can be used to describe the vapor phase. The liquid phase can either be described by an activity-coefficient model or by an EOS. The solid solution is often described by an activity-coefficient model (Prausnitz et al., 1986).

For vapor–liquid equilibria, it is common practice to use \( K \) factors, where \( K_i^{\text{v,l}} = y_i / x_i; \ y_i \) is the mole fraction in the vapor phase and \( x_i \) is the mole fraction in the liquid phase. It can readily be shown that \( K_i^{\text{v,l}} = \phi_i / \gamma_i \), where \( \phi \) is the fugacity coefficient as found from an EOS.

For solid–liquid equilibria, there is an analogous \( K \)-factor: \( K_i^{\text{s,l}} = x_i / x_i^s \). It can readily be shown that

\[
K_i^{\text{s,l}} = \frac{\gamma_i^s}{\gamma_i} \left( \frac{f_i}{f_i^s} \right)_{\text{pure}i},
\]

where \( \gamma \) is the activity coefficient. At any temperature and pressure, the ratio \( (f_i / f_i^s)_{\text{pure}i} \) can be calculated from the melting temperature, the melting enthalpy, and the heat capacities and densities of pure liquid \( i \) and pure solid \( i \), as discussed elsewhere (Prausnitz et al., 1986). The effect of pressure is usually negligible, unless the pressure is very high and/or the temperature very low.

As suggested in Figure 1, there is an alternate method for calculating \( K_i^{\text{v,l}} \). If the fugacity coefficient (\( \phi \)) in the liquid mixture is found from an EOS, while the solid phase is described by an activity coefficient model, then \( K_i^{\text{v,l}} = \phi_i^s / \gamma_i^s f_i^s / f_i^s \), where \( f_i^s \) and \( \phi_i^s \) are evaluated at the temperature and pressure of the mixture.

Won (1986) used two molecular thermodynamic models for describing the properties of the liquid phase. He used an EOS for computing \( \phi_i^s \) for vapor–liquid equilibria and a modified regular-solution model to estimate the nonidealities of the liquid and solid solutions, \( \gamma_i^s \) and \( \gamma_i^s \), respectively, for calculating liquid–solid equilibria. He neglected the effect of the heat-capacity difference of the solid and liquid, \( \Delta C_p \), on the ratio \( (f_i / f_i^s)_{\text{pure}i} \).

In 1989, Won used his method to calculate the solubilities of \( n-C_{28} \) and \( n-C_{36} \) solids in \( n-C_3 \) and \( n-C_{12} \) at atmospheric pressure. He modified his earlier model by (1) incorporating an extended regular-solution expression for activity coefficients in the liquid phase; (2) assuming a pure-solid phase for the heavier hydrocarbon component; and (3) including the heat-capacity effect on the ratio \( (f_i / f_i^s)_{\text{pure}i} \). The heat-capacity contribution improved prediction of the solubilities of the heavier \( n \)-alkanes in the liquid phase.

In 1988 Hansen et al. observed that Won’s model (1986) was not satisfactory for calculation of the cloud-point temperatures of 17 oil mixtures. They reasoned that since Won’s model gives activity coefficients close to unity for the wax-forming components, the \( K_i^{\text{v,l}} \)-factor of Eq. 2 essentially depends only on the ratio of \( f_i^s \) to \( f_i^s \). These authors proposed to use the polymer-solution theory of Flory (1953) for describing nonidealities in the liquid phase, and assumed \( \gamma_i^s = 1 \). Three adjustable parameters in the proposed model were estimated from measured cloud-point data. Using parameters from these data, agreement between calculated and experimental cloud points was good.

Extensive data on cloud-point temperature and amount-of-wax deposition became available in 1991. K. S. Pedersen et al. (1991) evaluated the performance of Won’s (1986) and Hansen et al.’s (1988) procedures with the data; these models significantly overestimated the amount of wax deposition and cloud-point temperature. To obtain an improved representation, K. S. Pedersen et al. (1991) proposed to modify Won’s model by (1) using solubility parameters \( \delta_i^L \) and \( \delta_i^d \) with one adjustable parameter for each of the solid and liquid phases; (2) incorporating the paraffinic/naphthenic/aromatic (PNA) split for each pseudocomponent of the \( C_7 \)-fraction; (3) modifying the melting-enthalpies of the \( P \), \( N \)- and A-pseudocomponents by means of one adjustable parameter; and (4) incorporating the effect of the heat-capacity difference, \( \Delta C_p \), on the computation of \( (f_i / f_i^s)_{\text{pure}i} \), with two-adjustable parameters. The five regression parameters were obtained by matching data and model results. This procedure revealed that (1) the solid solution is highly nonideal; and (2) the heat capacities strongly influence the solid deposition. While this model provided an improved representation of wax precipitation over previous procedures, it requires abundant experimental data for determining various model parameters.

To overcome the overestimation of wax deposition by available models, Pedersen (1993) recently suggested assigning high fugacity coefficients to selected components (pseudocomponents) of the crude oil. Based on an empirical relationship with constants estimated from experimental deposition data, Pedersen proposed that only a portion of the heptanes-plus fraction of an oil may coexist in solid–liquid equilibrium. Pedersen used the SRK-EOS (Soave, 1972) to describe gas and liquid phases and assumed the wax to be an ideal solid solution. Figure 2 illustrates the performance of Pedersen’s latest model for two oil mixtures (the compositions are in Table 1).

In this article, we present a thermodynamic method for wax precipitation with the assumption that wax deposition is a multisolid-phase process. Each solid phase is a pure component (or pseudocomponent); its existence or nonexistence is determined by phase-stability considerations. An EOS is used to describe properties of the gas and of the liquid. Calculated results are compared with experimental deposition data for binary model systems and for petroleum mixtures.

**Multisolid-Phase Model**

Recent reports in the literature describe the physics of solidification of crude-oil constituents below the cloud-point temperature. Solid-phase transitions and spontaneous demixing are parts of the wax-precipitation process. Differential-scanning-calorimetry studies by W. B. Pedersen et al. (1991) on a number of North Sea crude oils show phase transitions below the cloud-point temperature of various petroleum mixtures. Similarly, spectroscopic studies of Snyder et al. (1992, 1993, 1994) on the kinetics of microphase demixing of binary hydrocarbon mixtures show that the phase behavior below the cloud-point temperature of these systems follows an ini-
Figure 2. Measured vs. calculated wax-precipitation results for two petroleum mixtures at 1 bar.

Figure 3 shows a schematic separation vessel for a petroleum mixture that flashes into a vapor, a liquid, and several immiscible solid phases of pure components. The multisolid-phase model shown in Figure 3 is best illustrated by a plot of wax precipitated vs. temperature, shown in Figure 4. Below the cloud-point temperature, the precipitation of wax constitutes a consecutive deposition process that precipitates several pure solids, each completely immiscible with the others in the solid state. At a given temperature, the total amount of precipitated wax is the sum of the contributions of all solid phases that exist in equilibrium with the liquid at that temperature.

Figure 4. Multisolid-phase precipitation concept for a petroleum mixture below its cloud-point temperature.
From stability considerations, it follows that (pseudo) component $i$ may exist as a pure solid if

$$f_i(P, T, z) - f_i^\text{pure}(P, T) \geq 0, \quad (i = 1, 2, \ldots, N),$$

where $f_i(P, T, z)$ is the fugacity of component $i$ with feed composition $z$. This stability criterion is easily derived from Eq. 5 of Michelsen (1982). The mixture components that fulfill the preceding expression will precipitate, while those that do not will only be present in the liquid and vapor states. The Peng–Robinson EOS (Peng and Robinson, 1976) in the form described by Robinson et al. (1985) is used for calculating fugacities for components in the fluid phases.

**EOS Modeling**

At fixed temperature and pressure, for every component $i$, the multisolid–phase model must satisfy

$$f_i^f = f_i^l = f_i^\text{pure}, \quad (i = N - (N_i - 1), \ldots, N) \quad (4)$$

$$f_i^g = f_i^l \quad (i = 1, 2, \ldots, N - N_i), \quad (5)$$

where $N_i$ is the number of solid phases determined from Eq. 3. Coupling material balances with Eqs. 4 and 5, there will be a set of $N_i + 2N - 1$ simultaneous equations with $N_i + 2N - 1$ unknowns (see the Appendix). If no vapor phase is present, the model reduces to $N_i + N - 1$ variables. This multiphase-flash problem can be solved by Newton’s method.

As required for Eqs. 4 and 5, the fugacities in the vapor and liquid phases are evaluated through the EOS. The solid-phase fugacities of the pure components, $f_{i}^{\text{pure}, i}$, can be evaluated from the ratio $(f_i^f/f_i^l)^{\text{pure}, i}$. Neglecting the effect of pressure, this ratio is obtained from pure-component data for component $i$ as shown elsewhere (Prausnitz et al., 1986):

$$
\ln \left( \frac{f_i^f}{f_i^l} \right)^{\text{pure}, i} = -\frac{\Delta h_i^f}{RT} \left( 1 - \frac{T}{T_i^f} \right) \frac{1}{R} \int_{T_i^f}^{T} \frac{\Delta C_P}{T} dT - \frac{1}{R} \int_{T_i^f}^{T} \Delta C_P dT, \quad (6)
$$

where superscript $f$ refers to fusion. The liquid-phase fugacity is obtained from $f_{i}^{\text{pure}, i} = \varphi_{i}^{\text{pure}, i}(P, T) P$, where the fugacity coefficient, $\varphi_{i}^{\text{pure}, i}$, is obtained from the EOS. In Eq. 6, $T_i^f$ is the fusion (melting) temperature; $\Delta h_i^f$ is the enthalpy of fusion; and $\Delta C_P = C_P^f - C_P^l$, where $C_P^i$ is the heat capacity of pure $i$ at constant pressure. For hydrocarbons and petroleum mixtures, a simple cubic EOS such as the PR-EOS described in the EOS book describes the liquid and gas phases well (away from the gas–liquid critical region, cf. Firoozabadi, 1988).

The flash calculation proceeds as follows:

(a) Characterize the plus fraction of a given petroleum mixture using, say 7 to 12 pseudocomponents. Assign critical properties andacentric factors to all the pseudocomponents using available correlations. In this work, we used the correlations proposed by Cavett (1964), but other similar methods (Twu, 1984; Riazi and Daubert, 1980) may be used.

(b) For hydrocarbon pairs, use the component critical volumes, $V_{ci}$, to compute the values of binary interaction parameters for the EOS, $k_{ij}^{EOS}$, from the correlation of Chueh and Prausnitz (1967):

$$k_{ij}^{EOS} = 1 - \frac{2\Delta h_{ij}^{v}}{V_{i}^{l} + V_{j}^{l}} \quad (7)$$

Equation 7 is used to find the cross-parameter $a_{ij}$ in the EOS: $a_{ij} = (a_{ij})^{0.5} \sqrt{1 - k_{ij}^{EOS}}$. The critical volumes in Eq. 7 are estimated from the expression $V_{ci} = (RT_{ci}/P_{ci}) (0.290 - 0.085\omega_i)$, where $\omega_i$ is the componentacentric factor, as estimated from Edmister acentric factor formula (Edmister, 1958).

(c) Perform stability analysis (Eq. 3) for the feed at system temperature and pressure. Stability analysis gives the number and identities of the precipitating pure components (pseudocomponents) that form solid phases.

(d) Solve the system of equations described in the Appendix. For liquid–multisolid equilibria, the unknowns are $N_i$ solid-to-feed molar fractions, $S_i/F$, and $(N - 1)$ compositions in the liquid phase, $x_i$. For vapor–liquid–multisolid systems, the unknowns are $2(N - 1)$ compositions for the vapor and liquid phases, $y_i, x_i$, respectively, $N_i$ solid-to-feed molar phase fractions, $(S_i/F)$, and the fraction of feed that exists as vapor, $(V/F)$.

**Correlations for Calculating Fugacities of Pure Solids**

As shown by Eq. 6, the fugacity of solid-component $i$ depends upon the melting properties of component $i$: the melting-point temperature, $T_i^f$, the enthalpy of fusion, $\Delta h_i^f$, and the heat-capacity difference, $\Delta C_P$. In previous work, these quantities have been evaluated using different procedures. Unless stated otherwise, in this article the melting-point properties of the components were evaluated as follows.

**Melting-point temperature, $T_i^f$**

Won (1986) has given a correlation for the melting points of pure $n$-alkanes:

$$T_i^f = 374.5 + 0.026171 I_i - 0.02172 I_i, \quad (8)$$

where $T$ is in degrees kelvin and $I_i$ is molecular weight in grams per mole. To replace Eq. 8, we used experimental melting-point data of normal paraffinic ($C_{5}-C_{30}$), naphthenic ($C_{5}-C_{30}$ alkylcycloalkanes), and aromatic ($C_{6}-C_{30}$ alkylbenzenes) hydrocarbons (Research Project 44, API, 1964) to derive the following correlation (temperature in K):

$$T_i^f = 333.46 - 419.01 \exp(-0.0008546 I_i). \quad (9)$$

In the preceding equation, as the molecular weight increases, the calculated melting points of petroleum fractions gradually lose the paraffinic contribution. The asymptotic temperature relation of Eq. 9 corresponds to the average melting temperature of heavy naphthenic and aromatic hydrocarbons with carbon numbers above 30. Figure 5 shows Eq. 9 along with experimental data.
Enthalpy of fusion, $\Delta h_f$

Won (1986) developed a correlation for calculating the melting-point enthalpies of paraffinic hydrocarbons using the molecular weight of the paraffins as a characterization variable. The correlation has the form,

$$\Delta h_f = 0.1426 \frac{I}{T_f'},$$

where $\Delta h_f$ is the melting enthalpy, $I$ is the molecular weight, and $T_f'$ is the melting point.

The constant (0.1426) represents the average slope when the entropy of fusion, $\frac{(\Delta h_f/T_f')}{T_f'}$, is plotted against the molecular weight of paraffinic hydrocarbons. K. S. Pedersen et al. (1991) argued that the melting enthalpies of different hydrocarbon species found in a petroleum fluid have a broad range of values for the same molecular weight, and therefore Eq. 10 overestimates the wax amount below the cloud-point temperature. These authors concluded that Eq. 10 should not be applied to petroleum mixtures.

Figure 6 shows experimental data (Research Project 44, API, 1964) for the entropy of fusion of various P-, N- and A-hydrocarbons as a function of molecular weight. The melting enthalpies of n-paraffins are indeed higher than those of N- and A-hydrocarbons with the same molecular weight. However, when the slope of the entropy-of-fusion vs. molecular-weight line for normal paraffins given by Eq. 10 is decreased by a factor between 2 and 3, the resulting entropies tend to deviate from purely paraffinic behavior to a more “multiensemble” hydrocarbon environment, which may correspond more closely to the wax-precipitation context. Since the presence of paraffinic components decreases as the carbon number increases, smaller enthalpies of fusion than those proposed by Eq. 10 may be more representative for wax precipitation. A similar reduction process of the enthalpies of hydrocarbons was used by K. S. Pedersen et al. (1991) and by Erickson et al. (1993). We suggest the following expression for the enthalpy of fusion:

$$\Delta h_f = 0.05276 \frac{I}{T_f'},$$

where $\Delta h_f$ is in calories/mole.

Heat capacity of fusion $\Delta C_p$

Toward including the heat-capacity data, K. S. Pedersen et al. (1991) analyzed the trend of the experimental heat-capacity data with molecular weight for various n-alkanes and found that the data could be represented by the expression

$$\Delta C_p = \alpha I + \beta I T,$$

where $\Delta C_p$ is in calories/mole-K. Correlation coefficients $\alpha$ (0.3033 cal/g·K) and $\beta (-4.635 \times 10^{-4} \text{ cal/g·K}^2)$ were determined by K. S. Pedersen et al. by tuning their model with experimental precipitation data for 17 North Sea crude oils.

Here, we correlate heat-capacity data of heavy n-alkanes (Finke et al., 1954; Spaght et al., 1932) with molecular weight and temperature using the function given by Eq. 12. For the liquid phase below the melting point temperature, the heat capacity is assigned the value at the melting point. For the solid phase above the melting point temperature, the heat capacity at the melting point is assigned. By using this procedure, we found that the values of the correlation coefficients $\alpha$ and $\beta$ in Eq. 12 are close to those found by K. S. Pedersen et al. (1991). Therefore, we use their correlation coefficients. We also assume that hydrocarbon species other than n-alkanes follow Eq. 12 with the same coefficients. To test the validity of this assumption, thermal data of selected high-molecular-weight hydrocarbons other than n-alkanes (Parks et al., 1949; Fischl et al., 1945) were compared with predictions from Eq. 12. The predicted heat-capacity differences were 10 to 20% higher than the heat capacity data of heavy naphthenic and aromatic hydrocarbons. Therefore, the heat capacity correlation given by Eq. 12 appears to provide a reasonable estimate for the thermal effects on the fugacities of solid-forming components in petroleum mixtures.


Results

Binary systems

Madsen and Boistelle (1976, 1979) measured binary solid solubilities of six n-alkane mixtures (n-C₃₆ in n-C₅, n-C₃₆ in n-C₆, n-C₃₂ in n-C₇ and n-C₁₂, n-C₃₆ in n-C₄, and n-C₃₆ in n-C₆). For normal paraffins, we used the n-alkane-based correlations for estimating the melting-point temperature and enthalpy of fusion given by Won (Eqs. 8 and 10). Figures 7 and 8 show calculated and experimental results. Figure 7 shows that the calculated solubilities are predicted very well for all systems. The effect of the heat-capacity data on calculated results is illustrated in Figure 8 for systems n-C₃₂ in n-C₇ and n-C₃₆ in n-C₆. Including the $\Delta C_p$ term provides a significant improvement. A similar effect was observed for other binary systems. The results shown in Figures 7 and 8 are predicted without any parameter adjustment.

Crude-oil systems

Table 1 shows compositions, component molecular weights, and plus-fraction-specific gravities of eight petroleum mixtures. W. B. Pedersen et al. (1991) have provided extensive data on wax-formation behavior of these crude oils. The mixture numbers are the same as those used by these authors. The types of crude oils shown in Table 1 cover a variety of oil mixtures. Mixtures 10, 12, and 15 originate from light petroleum systems of the gas-condensate type. Mixtures 8 and 11 originate from heavy oils. For calculation purposes, the plus fractions in all mixtures require a systematic characterization procedure. For each oil, we used the experimental molecular weight, mole fraction, and specific-gravity data of the plus fraction to generate a number of pseudocomponents that preserve the measured characterization properties of the heavy fraction. The carbon-number distribution of petroleum waxes has been studied by some investigators. Ronningsen et al. (1991) reported wax composition of a given crude from carbon number C₁₆ to much higher carbon numbers. They estimated C₄₀₊ content of a particular wax to be around 50% (volume). They also cautioned that the wax that they analyzed inevitably contained some trapped oil that affects the lower carbon number. In 1994, Bishop and Philp, using a high-temperature gas chromatographic technique, have shown that the spectrum of hydrocarbon components found in petroleum waxes begins at approximately C₂₀–₂₅ but, unlike Ronningsen et al. (1991), Bishop and Philp analyzed the fraction of hydrocarbon components beyond C₄₀ and found that the carbon-number distribution extends to C₉₀–₁₀₀. From these two studies, it is evident that for precipitation calculations, a pseudocomponent slate with components whose molecular weights exceed 1,000 is desirable. The two-parameter gamma distribution function (Johnson and Kotz, 1970; Whitson, 1983) was used for generating the molar distributions for the plus fractions of each of the eight petroleum
mixtures of Table 1. Figure 9 shows the shape of the molar distributions for all mixtures, and Table 2 shows the distribution-function parameters for each fraction. Table 3 shows the resulting characterization parameters for the heptanes-plus fraction of Oil 1.

Figures 10 and 11 show results using our multisolid-phase model. These figures indicate that the multisolid-phase assumption appears to represent the wax-formation process in real petroleum mixtures. For all mixtures, the predicted trend for the solid amount with temperature is in good agreement with experiment. At a given temperature, the wax weight percent that precipitates from crude oil is calculated for 1 mol of feed from the relation

\[
\text{Wax weight} \% = \left( \frac{\text{total precipitated mass}}{\text{mass of feed oil}} \right) \times 100
\]

Table 1. Compositions and Properties of Oil Mixtures

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*C<sub>20</sub> or C<sub>21</sub>.

Figure 9. Estimated molar distribution for plus fractions of oil mixtures.
Predictions for Oils 10, 12 and 15, which originate from gas-condensate mixtures, are as good as those for Oils 8 and 11, which originate from heavy-petroleum systems.

Equation 3 provides a useful criterion for determining those components that precipitate. Application of the stability test for all the mixtures revealed that, for temperatures in excess of 230 K, hydrocarbon components with molecular weights less than, say 400, are unlikely to participate in the solid wax. For Oil 1, up to four different solid phases characterize the predicted wax weight percent along the indicated temperature range. These four solids consist of pseudocomponents with average molecular weights 750, 800, 950 and 1350, respectively (Table 3). Similar molecular weights characterize the solid phases for the other systems. The model proposed in this study suggests that, in typical real systems, the "carrying" capacity of the light fraction of the oil keeps hydrocarbons with molecular weights ranging from 100 (C18) to around 400 (C25) dissolved in the liquid phase (oil), in agreement with the wax analysis by Bishop and Philp (1994). The solid-solution models predict the presence of light hydrocarbons in the solid wax (Won, 1989).

Figure 12 shows the solid-phase-appearance history of Oil 1. As cooling proceeds, the multisolid-phase model predicts the appearance of solid phases along the experimental temperature range in a consecutive manner, as illustrated in Figure 4. From our experience, the more discontinuous the experimental precipitation curve of a particular oil (as occurs for Oils 2 and 15), the larger the number of precipitated phases predicted by the model (8 and 12 solid phases, respectively). On the other hand, for fluid systems showing an abrupt jump in the experimental precipitation-vs.-temperature curve (Oils 5 and 11), a small number of precipitated solid phases provides a good representation of the data. The characterization technique employed here for wax calculations differs from the conventional characterization schemes for hydrocarbons.

### Table 2. Statistical Properties for Molar Distributions of Oil Mixtures

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<th>Initial mol wt.</th>
<th>Mean</th>
<th>Variance</th>
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### Table 3. EOS-Characterization for the Heptanes-Plus Fraction of Oil 1

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<th>No.</th>
<th>mol %</th>
<th>mol. wt.</th>
<th>Tc/K</th>
<th>Pc/bar</th>
<th>ω</th>
<th>Vc/cm³/mol</th>
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tested with experimental data. The method is based on the experimentally supported assumption that wax precipitation is a multisolid-phase precipitation process. The number and identity of the potential precipitated phases can be determined by a simple stability test. Application of this method to several petroleum mixtures suggests that the precipitated waxy material consists of high-molecular-weight hydrocarbons with average carbon-atom numbers above 25. Calculated results of the new method reproduce experimental liquid-wax equilibria for several oil mixtures, indicating that the proposed method is both simple and accurate, requiring no adjustable mixture parameters.

**Acknowledgments**

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**Notation**

\[ \begin{align*}
K &= \text{partition coefficient} \\
L &= \text{moles of liquid phase} \\
P &= \text{pressure} \\
R &= \text{gas constant} \\
S &= \text{moles of solid phase} \\
v &= \text{molar volume} \\
x &= \text{solid composition, depending on superscript} \\
z &= \text{overall (feed) mole fraction} \\
\Sigma &= \text{sum operator} \\
\end{align*} \]

**Subscript**

\[ c = \text{property at the critical point} \]

**Literature Cited**


Appendix: Model Formulation

Consider a system of \( N_s \) precipitating species, and \( N \) components. The equations of phase equilibria are

\[
\begin{align*}
(1) \quad N & \quad \text{vapor-liquid isofugacity equations} \\
 f^{(1)}(P,T,y_1, y_2, \ldots, y_{N-1}) - f^{(L)}(P,T,x_1, x_2, \ldots, x_{N-1}) = 0 \\
 & \quad (i = 1, \ldots, N). \\
(2) \quad N_s & \quad \text{liquid-solid isofugacity equations} \\
 f^{(L)}(P,T,x_1, x_2, \ldots, x_{N-1}) - f^{(S)}(P,T) = 0 \\
 & \quad [(i = (N - N_s) + 1, \ldots, N)]. \\
(3) \quad N - 1 & \quad \text{material-balance equations} \\
 \end{align*}
\]

(a) For the nonprecipitating components:

\[
\begin{align*}
\sum_{i=1}^{N} \frac{N_i}{F} x_i^\ell y_i & \quad \text{(1) for precipitating components, where all solid phases are pure:} \\
\sum_{i=1}^{N - N_s} \frac{N_i}{F} x_i^\ell y_i & \quad \text{(4)}.
\end{align*}
\]

where \( K^\ell = \frac{\psi(P,T,x^\ell)}{\psi(P,T,y)} \).

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